Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 36 (2013) 1192 – 1201

Energy Procedia

TerraGreen 13 International Conference 2013 - Advancements in Renewable Energy and Clean Environment

Lifetime analysis of a hydrogen generator by hydrolysis of sodium borohydride

T. Vilarinho-Franco[a,b*], R. Tenu[b], J. Delmas[a], M. Heitzmann[a], P. Capron[a], C. Goutaudier[b]

[a]*Laboratoire LITEN-DTNM-LCSN, CEA - Commissariat à l'énergie atomique et aux énergies alternatives de Grenoble, 17, rue des Martyrs 38054 Grenoble cedex 9, France*

[b]*Laboratoire Multimatériaux et Interfaces, Université Claude Bernard Lyon 1, UMR CNRS 5615, 69622 Villeurbanne cedex, France*

Abstract

The interesting point of this work is to increase the amount of produced H_2 in order to improve the energy density of the H_2 generator system. For this, one of the main challenges is to increase the $NaBH_4$ concentration of the cartridge solution thus avoiding the drawbacks induced by $NaBO_2$ crystallization, but also to control the stability of this solution, it means add sodium hydroxide to limit the $NaBH_4$ self-decomposition, thus stabilizing the system. This paper shows the two aspects of the cartridge lifetime analysis: the overall order reaction of spontaneous hydrolysis reaction of alkaline aqueous $NaBH_4$ solutions as function of NaOH concentration and the operation temperature range of the cartridge; an unequivocal understanding of the $NaBO_2$ crystallization process and more specifically the delimitation of the homogeneous liquid phase domain in the quaternary system $NaBH_4$–$NaBO_2$–NaOH–H_2O.

Keywords: hydrogen generation; spontaneous sodium borohydride hydrolysis; kinetic analysis; solid-liquid equilibria

1. Introduction

Numerous investigations are addressing both component optimization and development of miniature energy sources.

* Corresponding author. Tel.: + 33 (4) 38 78 02 54.
E-mail address: tatiana.vilarinho-franco@cea.fr

doi:10.1016/j.egypro.2013.07.135

Nomenclature

ΔP	pressure variation, *bar*
k	overall kinetic constant
P_{mes}	measured pressure, *bar*
P_{ref}	reference pressure, *bar*
V_{free}	free volume of the bench, cm^3
V_{H2}	volume of produced hydrogen, cm^3
V_{molar}	molar volume
V_{sol}	volume of the solution
R	gas constant
T	temperature
t	time, *h*
n	overall order reaction
N_A	borohydride mol number
N_{A0}	borohydride initial mol number
w^J	mass fraction in Jänecke coordinates

The rise of portable electronic devices, brings to the fore the crucial issues of power supply. The foreseeable evolution in functionalities and utilizations, as regards portable electronic devices, together with the introduction of novel electronic components, entail considerable changes in requirements, in terms of power consumption and autonomy (Fig. 1) [1].

A hydrogen system for its production and distribution depends on the type of hydrogen storage used. This gas has a very low volumetric energy density, so it is difficult to store a sufficient amount of it in a small and light enough vessel. In fact, a safe, efficient and economical method of storing hydrogen must be available to turn viable a hydrogen economy based on renewable resources [2-4].

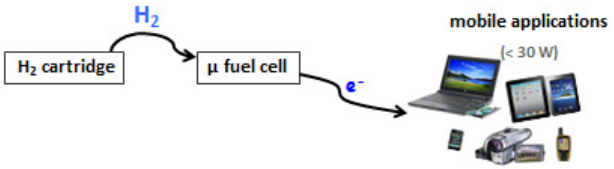

Fig. 1. Global process scheme of H_2 generator and micro-fuel cell to mobile applications.

Hydrogen generation by means of the hydrolysis of borohydrides is a promising technology for portable fuel cells [5-8]. Particularly, sodium borohydride ($NaBH_4$) presents many advantages for that purpose. For example, $NaBH_4$ solutions are non-flammable thus yielding safe processes; the rate of H_2

generation is easily controlled by a catalyst; reaction products are environmentally benign and finally the reaction by-product can be recycled.

The hydrolysis of $NaBH_4$ in water to produce H_2 gives by-products, $NaBO_2.yH_2O$, hydrated sodium borate compounds according to the sodium borohydride hydrolysis reaction Eq. 1, with the pseudo hydration degree y = 0, 1/3, 2/3, 2 or 4 [9].

$$NaBH_{4(s)} + (2+y)H_2O_{(l)} \Leftrightarrow 4H_{2(g)} + NaBO_2.yH_2O_{(s)} \quad (1)$$

The exponential growth of the $NaBH_4$ hydrolysis rate with decreasing *pH* is known for weakly alkaline concentrations. The spontaneous hydrolysis of pure $NaBH_4$ solution is an acid-catalysed reaction, H_3O^+ ions are formed in-situ. A detailed mechanism based on the substitution of B-H bonds by B-OH in aqueous solutions leading to the formation of borate and hydrogen, has been proposed by Mochalov et al. [10]. This mechanism presents the steps of the hydrolysis reaction and the formation of different intermediates.

The hydrolysis would be a multistep process involving hydroxyborate intermediates $BH_{4-z}(OH)_z$ (z from 1 to 3) [11]. Mochalov et al. have verified the formation of these hydroxy derivatives by subjecting a solution of $NaBH_4$, which was undergoing hydrolysis, to chromatographic separation on paper under conditions of a strongly alkaline medium.

The reactions (Eq. 2) show the H_3O^+ catalyzed hydrolysis of $(BH_4)^-$ and the formation of the first intermediate $BH_3(OH)^-$; z = 1. The formation of BH_3 from $(BH_4)^-$ involves an activated complex. The Eq. 2 presents the steps of activated complexes formation, the limiting steps of the hydrolysis's mechanism [11].

The participation of the OH^- ions in the hydrolysis process sets in with the stage for the formation of borine (diborane), BH_3, which being a strong Lewis acid, readily takes on OH^- to form a more stable ion, BH_3OH^-. Mochalov et al. affirms that these reactions take place very rapidly since the particles BH_3, BH_2OH and $BH(OH)_2$ are most unstable and very reactive. So, it may be seen that an aqueous solution of borohydride is a very complex system of many components [10].

$$\begin{aligned} BH^-_{4\,(aq)} + H_3O^+{}_{(aq)} &\rightarrow BH_{3(aq)} + H_2O_{(l)} + H_{2(g)} \\ BH_{3(aq)} + OH^-{}_{(aq)} &\rightarrow BH_3OH^-{}_{(aq)} \end{aligned} \quad (2)$$

The theoretical hydrogen yield in the reaction in Eq. 1 is 10.8 w% if the selectivity of by-products is displaced to the anhydrous borate (y = 0). However, anhydrous borate is obtained only under extreme temperature or pressure conditions, which are incompatible with portable applications. Moreover, water in excess is required to solubilize the reaction by-product in order to avoid any crystallization phenomena on the catalyst surface, a condition which may affect the hydrogen generation rate. Consequently, an unequivocal understanding of the $NaBO_2$ crystallization process remains to be a key factor. It is not reliable to approximate the H-content by simply assuming the theoretical yield and, thus being required to consider equilibrium and thermophysical properties such as the solubility limit, density, viscosity and the formation of crystalline by-products [12].

The present paper has the intent to study two aspects of the cartridge lifetime. Firstly, this work presents an overall order reaction of spontaneous hydrolysis of alkaline aqueous $NaBH_4$ solutions

(14.0 w%) for NaOH concentration of 4.0 w% at 50 °*C*. Secondly, a study about the $NaBO_2$ crystallization process will be present, more specifically, the delimitation of the homogeneous liquid phase domain in the quaternary system which represents the solution during the cartridge operation.

2. Material and methods

2.1. Solutions stability: Spontaneous sodium borohydride hydrolysis

Hydrogen generation is obtained by the measurement of the relative pressure in a stainless bench (Swagelok) (Fig. 2).

The molar volume of a perfect gas is 24000.0 $cm^3.mol^{-1}$ at $T = 20$ °*C* and $P = 1.0$ *atm*. The pressure variation of the hydrogen generation has been measured at these conditions. The pressure sensor accuracy is 0.3% of the sensor range, for the experiments at 20 °*C* the sensor range is from 0 to 5 *bar* ± 0.0015, and, for the experiments at 50 and 70 °*C* it is from 0 to 20 *bar* ± 0.006.

The volume of generated hydrogen, considering an ideal gas, is calculated by the Eq. 3.

$$V_{H_2\,prod} = n_{H_2\,prod}.V_{molar} = \frac{\Delta P.V_{free}.V_{molar}}{R.T} \text{ ; with } \Delta P = P_{mes} - P_{ref} \quad (3)$$

For each solutions preparations, anhydrous NaOH (Sigma-Aldrich®, ≥ 99.99 % purity, pellets, n° CAS: 1310-73-2) and $NaBH_4$ (Sigma-Aldrich®, 98 % purity, caplets, n° CAS: 16940-66-2) are stored and handled in an argon-filled glove box in order to prevent hydration, thus avoiding moisture and subsequent hydrolysis, in the case of the $NaBH_4$. Deionized water is introduced at room temperature in order to avoid spontaneous decomposition of $NaBH_4$ in water. After homogenization of the solution, a sample is added to the reactor of the stability bench (Fig. 2).

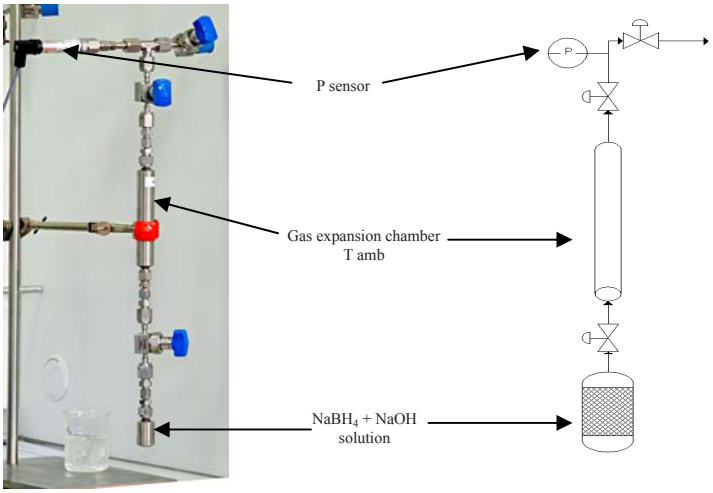

Fig. 2. Stability bench for hydrogen generation by spontaneous $NaBH_4$ hydrolysis.

2.2. Solubility in the quaternary system $NaBH_4$–$NaBO_2$–NaOH–H_2O

For each quaternary mixture preparations, anhydrous NaOH (Sigma-Aldrich®, ≥ 99.99 % purity, pellets, n° CAS: 1310-73-2) and $NaBH_4$ (Sigma-Aldrich®, ≥ 99% purity, powder, n° CAS: 16940-66-2) are stored and handled in an argon-filled glove box in order to prevent hydration, thus avoiding moisture and subsequent hydrolysis, in the case of the $NaBH_4$. Deionized water is introduced at room temperature in order to avoid spontaneous decomposition of $NaBH_4$ in water. Sodium borate can be by heat treatment of the $NaBO_2.yH_2O$ (ACROS Organics, 98.5 % purity, n° CAS: 10555-76-7) in order to obtain the $NaBO_2$ anhydrous. In this latter case, commercial borate (a mixture of $NaBO_2.4H_2O$ and $NaBO_2.2H_2O$) is heated at 300 °*C* for 72 hours in a tubular oven under argon flow. Afterwards, anhydrous borate is confirmed by X-ray diffraction analysis. Then, for each mixture, a solution of 30-50 g is prepared in order to have enough liquid sample for chemical analysis after centrifugation and decantation processes. The experimental procedure is as follows: Weigh the desired amount of anhydrous NaOH, $NaBO_2$ and $NaBH_4$ in a plastic centrifuge tube. Add the exact amount of water. Introduce a stir bar in the solution tube and, then, insert it in a thermostated reactor, where the solution is stirred during 30 minutes which is sufficient to reach the equilibrium state. Thermostated centrifugation of the solution until obtaining the separation of phases (liquid + solid). Lastly, in addition, a thermostated decantation is performed before chemical analysis to further attain a complete separation of phases.

In order to determine the solubility limit, the liquid phase is analysed by acid-base titration with HCl (0.5 $mol.L^{-1}$). A classic acid-base titration curve is obtained with two equivalence points, the first one corresponding to NaOH while the second one corresponds to $NaBO_2$. $NaBH_4$ content in the saturated liquid phase of quaternary solutions is quantified by means iodometric titration. Besides establishing the NaOH amount; acid-base titration gives the total $NaBO_2$ amount (i.e. the $NaBO_2$ content in the saturated solution together with the amount produced by consumption of $NaBH_4$ during HCl titration). The $NaBO_2$ amount present in the saturated liquid phase solution is obtained then by difference.

The determination of the solid phase in equilibrium with the liquid is performed by means of X-ray diffraction (XRD). XRD analyzes are performed on the Bruker D8 Advance diffractometer, in air, at room temperature. This diffractometer has a Bragg-Brentano configuration, used in reflection mode, with a θ-2θ installation and a copper anticathode tube ($\lambda K\alpha 1 = 1.5406$ Å - $\lambda K\alpha 2 = 1.54439$ Å) . The sample is prepared by removing some solid phase from the biphasic solution. The solid sample is dried with a filter paper to remove the solution. Then it is deposited on a specific holder. Kapton® is used to prevent hydration of the solid during sample handling and analysis.

3. Results

3.1. Solution stability: Spontaneous sodium borohydride hydrolysis

3.1.1. Temperature dependence

The Fig. 3 compares the volume of hydrogen generation at different temperatures: 20, 50 and 70 °*C* for 3.0 w% NaOH and $NaBH_4$ composition of 14.0 w% (initial conditions). The hydrogen generation volume increases as temperature increases at a fixed NaOH concentration, as expected.

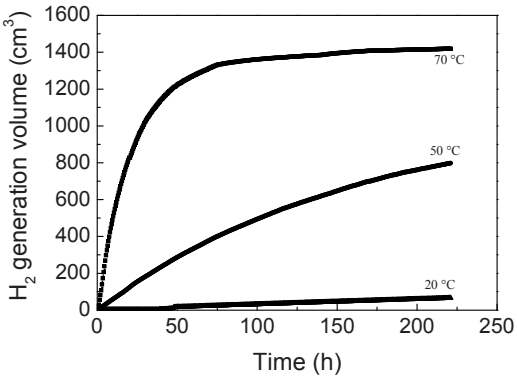

Fig. 3. Volume of hydrogen generation as a function of time at 20, 50 and 70 °C, 3.0 w% NaOH and 14.0 w% $NaBH_4$.

The Fig. 3 illustrates that the volume of generated hydrogen is strongly dependent on temperature and the behavior of this curve changes enormously for high temperatures, and this behavior justifies a carefully evaluation of the kinetic parameters, in particular for a long operating time.

3.1.2. Empirical Rate Equations of $NaBH_4$ hydrolysis

Thermal decomposition of borohydride in alkaline solution is assumed by different authors to be a first-order reaction, as a function of $NaBH_4$ [13]. It is evident it is a complex mechanism like it has been presented by Mochalov et al.

At this work, the *pH* of the solutions is always superior to 13.0 because of the presence of the stabilizer agent, NaOH, it means, a non-catalytic hydrolysis, with a slow *pH*-independent path. In this case, there is no data about the mechanism in the literature, and an empirical rate equation of *n*th order has been applied with the intent to fit the data with an *n*th-order rate equation of the form:

$$-r_A = -\frac{dC_A}{dt} = k.C_A^n \tag{4}$$

Some hypotheses for the overall order of the hydrolysis reaction, *n*, have been evaluated. The Eq. 5 presents the variation of $NaBH_4$ mol number, N_A, as a function of time, for a constant volume of solution during hydrolysis reaction.

$$V_{sol} = cte \quad \text{then :} \quad -\int \frac{dN_A}{N_A^n} = k.V_{sol}^{(1-n)} \int dt \tag{5}$$

$n = 0, 1, 2, 5/2, 3$

Churikov et al. established some characteristics of the kinetic curve of borohydride hydrolysis in strongly aqueous solutions (content of NaOH from 8.24 to 27.32 w%). A fast initial decomposition by a linear law (zero-order reaction) with a gradual transfer to slow decomposition (the logarithmic law) at middle stages (first-order reaction) [13].

In a first moment, the hypothesis of a first-order reaction, for hydrolysis conversion < 40 %, has been evaluated (Eq. 6). The Table 1 shows the kinetic constant, *k*, as a function of [NaOH] for the subsequent retarded decomposition regime described by the logarithmic law. For the experimental results at 50 °*C*, 40 % conversion is achieved around 200 hours, although at 70 °*C*, 40 % conversion is achieved around 30 hours.

$$\ln\left(\frac{N_{A0}}{N_A}\right) = f(t) \tag{6}$$

Table 1. Kinetic constants of the hydrolysis reaction conversion < 40 %, hypothesis of a first-order reaction.

NaOH (w%)	*50 °C*		*70 °C*	
	k (h^{-1})		*k* (h^{-1})	
2.0	$4.40x10^{-3}$	r^2 =0.997	$3.976x10^{-2}$	r^2 =0.998
3.0	$3.60x10^{-3}$	r^2 =0.994	$3.220x10^{-2}$	r^2 =0.995
4.0	$2.95x10^{-3}$	r^2 =0.995	$2.215x10^{-2}$	r^2 =0.993

After this hypothesis of a first-order reaction for hydrolysis conversion < 40 %, it has been decided to evaluate an overall order reaction between 1 and 3 to describe the totally of the experimental curve at 50 °*C*, ie for a period of about 700 hours of continuous operation. For this evaluation, the NaOH content of 4.0 w% has been chosen.

The variation of the number of moles versus time has been expressed for different overall order reaction and a linear relation is expected. For this purpose, the hypotheses of an overall order reaction have been evaluated. The Fig. 4-9 illustrate the relation between the variation of $NaBH_4$ mol number as a function of time submits to the hypotheses of order reaction: 1, 2, 3 and 5/2, respectively.

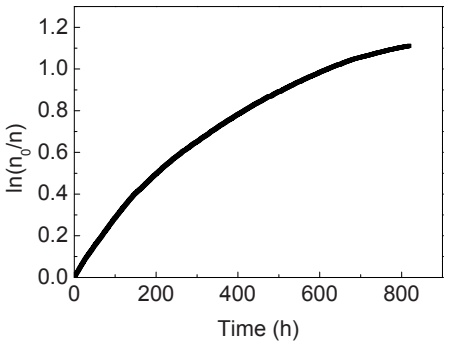

Fig. 4. Borohydride decomposition degree as a function of time at 50 °*C* and 4.0 w% NaOH, an overall first-order hypothesis.

The Fig. 4 presents the hypotheses of first-order reaction and a non-linear relation has been obtained, it means that the totally of the curve can not be described as a first order-reaction, even though different authors have affirmed this. The hypotheses of second and third order have been evaluated and it is possible to note that a better linear correlation is obtained to an overall order reaction between 2 and 3 (Fig. 5 and 6, respectively). An overall 5/2 order reaction presents a satisfactory linearization for the experimental curve at 50 °*C*, with a good correlation coefficient, $r^2 = 0.9998$ (Fig. 7).

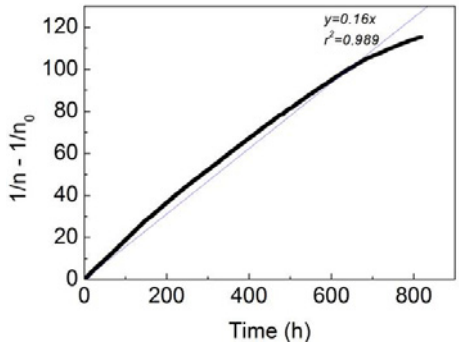

Fig. 5. Borohydride decomposition degree as a function of time at 50 °*C* and 4.0 w% NaOH, an overall second-order hypothesis.

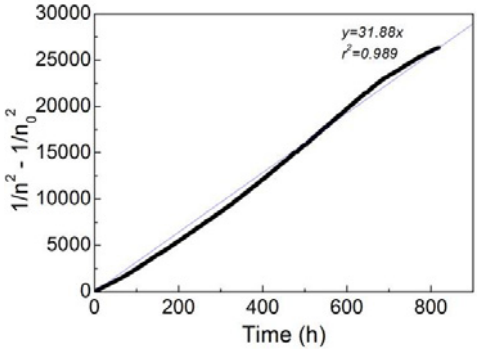

Fig. 6. Borohydride decomposition degree as a function of time at 50 °*C* and 4.0 w% NaOH, an overall third-order hypothesis.

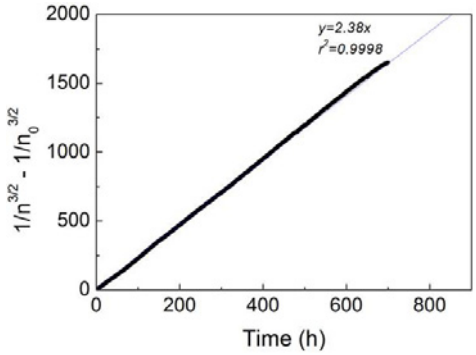

Fig. 7. Borohydride decomposition degree as a function of time at 50 °*C* and 4.0 w% NaOH, an overall 5/2 order hypothesis.

3.2. Solubility in the quaternary system $NaBH_4$–$NaBO_2$–NaOH–H_2O

To determine the solubility limit of the solid phases in the quaternary system, an isoplethic section has been defined considering a constant NaOH composition.

The Figure 8 depicts the quoted isoplethic section of the quaternary system.

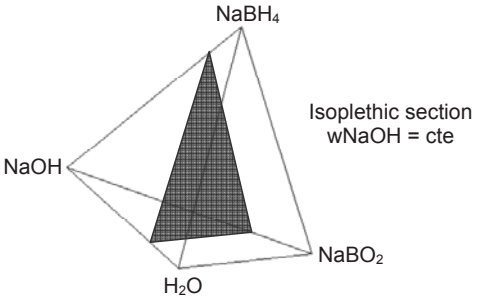

Fig. 8. Isoplethic section for a constant NaOH composition of the quaternary system at isobaric and isothermal conditions.

Figure 9 presents detailed experimental results of the solubility limit at 0 °*C* and 20 °*C* for the quaternary system at the isoplethic section.

The isotherm at 20 °*C* in Figure 9 illustrates three biphasic regions: Liquid + $NaBO_2.4H_2O$, Liquid + $NaBO_2.2H_2O$, and Liquid + $NaBH_4.2H_2O$; and two triphasic regions: L_1 + $NaBO_2.4H_2O$ + $NaBO_2.2H_2O$ and L_2 + $NaBO_2.2H_2O$ + $NaBH_4.2H_2O$. Although the isotherm at 0 °*C* illustrates two biphasic regions: Liquid + $NaBO_2.4H_2O$ and Liquid + $NaBH_4.2H_2O$; and one triphasic region: L_0 + $NaBO_2.4H_2O$ + $NaBH_4.2H_2O$. All these solid phases have been confirmed by XRD.

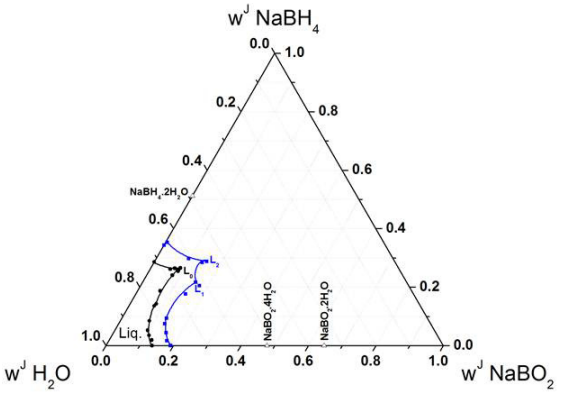

Fig. 9. Solubility limit at 0 °*C* (black) and 20 °*C* (blue) of the quaternary system $NaBH_4$–$NaBO_2$–H_2O–NaOH (mass fraction in Jänecke coordinates, w^J) for an isoplethic section considering a constant NaOH composition (*P* = 1 *atm*).

4. Conclusion

This work contributes for a lifetime analysis of a hydrogen generator involving the stability of the solution and the solubility limit of the quaternary system $NaBH_4$–$NaBO_2$–NaOH–H_2O.

An initial part of this work proposes a kinetic analysis of experimental curves of the spontaneous hydrolysis of concentrated $NaBH_4$ solutions with the stabilizer agent NaOH. The hypothesis of a first-order reaction for a hydrolysis conversion inferior to 40 % has been evaluated at 50 and 70 °*C* and for 2.0, 3.0 and 4.0 w%. NaOH. An overall 5/2 order reaction has been revealed for the entire experimental curve at 50 °*C*. A fractional order of a chemical reaction gives the evidence of a kinetic mechanism, which allows to reaffirm that an aqueous solution of borohydride is a very complex system of many components.

A second part presents the experimental results of the solubility limit at 0 °*C* and 20 °*C* of the quaternary system for a constant NaOH concentration, showing the decrease in the volume of liquid by lowering the temperature.

References

[1] CEA - Commissariat à l'énergie atomique et aux énergies alternatives: The Hydrogen Pathway <http://www.cea.fr/var/cea/storage/static/gb/library/Clefs50/pdf/094a095marsacq-gb.pdf> (accessed Oct 11, 2012).

[2] M.J.F. Ferreira, L. Gales, V.R. Fernandes, C.M. Rangel, A.M.F.R Pinto. Alkali free hydrolysis of sodium borohydride for hydrogen generation under pressure. *Int. J. of Hydrogen Energy* 2010;**35**:9869–9878.

[3] S.C. Amendola, S.L. Sharp-Goldman, M.S. Janjua, M.T. Kelly, P.J. Petillo, M. Binder. A safe hydrogen generator using aqueous borohydride solutions. *J. of Power Sources* 2000;**85**:186.

[4] L. Damjanović, S. Bennici, A. Auroux. A direct measurement of the heat evolved during the sodium and potassium borohydride catalytic hydrolysis. *J. of Power Sources* 2010;**195**:3284-3292.

[5] J. Delmas, L. Laversenne, I. Rougeaux, P. Capron, A. Garron, S. Bennici, D.Świerczyński, A. Auroux. Improved hydrogen storage capacity through hydrolysis of solid $NaBH_4$ catalyzed with cobalt boride . *Int. J. of Hydrogen Energy* 2011;**36**:2145–2153.

[6] Liu B.H., Li Z.P., A review: Hydrogen generation from borohydride hydrolysis reaction. *J. of Power Sources*, 2009;**187**:527–534.

[7] Marrero-Alfonso E. Y., Gray J. R., Davis T. A., Matthews M. A., Minimizing water utilization in hydrolysis of sodium borohydride: The role of sodium metaborate hydrates, *Int. J.of Hydrogen Energy* 2007;**32**:4723-4730.

[8] Ç. Çakanyildirim and M. Gürü, Hydrogen cycle with sodium borohydride, *Int. J. of Hydrogen Energy* 2008;**33**:4634–4639.

[9] J. Andrieux, L. Laversenne, O. Krol, R. Chiriac, Z. Bouajila, R. Tenu, J.J. Counioux, C. Goutaudier. Revision of the $NaBO_2$–H_2O phase diagram for optimized yield in the H_2 generation through $NaBH_4$ hydrolysis. *Int. J. of Hydrogen Energy* 2012;**37**:5798–5810.

[10] K.N. Mochalov and V.S. Khain. Generalized scheme for the hydrolysis of the borohydride ion and diborane. Tr. Kazansk. Khim.-Tekhnol. Inst. 1964;**33**:79–85.

[11] J. Andrieux, U. B. Demirci, J. Hannauer, C. Gervais, C. Goutaudier, P. Miele. Spontaneous hydrolysis of sodium borohydride in harsh conditions. *Int. J. of Hydrogen Energy* 2011;**36**:224–233.

[12] S. Suda, Y-M. Sun, B-H. Liu, Y. Zhou, S. Morimitsu, K. Arai, N. Tsukamoto, M. Uchida, Y. Candra, Z-P. Li. Catalytic generation of hydrogen by applying fluorinated-metal hydrides as catalysts. *Appl. Phys. A* 2001;**72**:209–212.

[13] A. V. Churikov, I. M. Gamayunova, K. V. Zapsis, M. A. Churikov and A.V. Ivanishchev. Influence of temperature and alkalinity on the hydrolysis rate of borohydride ions in aqueous solution. *Int. J. of Hydrogen Energy* 2012;**37**:335–344.